	FOR OFFICIAL USE National Qualificatio 2023	ons			Mark	
X813/77/01			Sect	ion 1 —	Chei - Answe and Sec	mistry er grid tion 2
FRIDAY, 12 MAY				11		
9:00 AM – 12:00 NOON				∥ *	× X 8 1 3 7	701*
Fill in these boxes and read Full name of centre	d what is printed	below.	Town			
Forename(s)	Surna	ame			Number	of seat
Date of birth Day Month	Year	Scottish ca	andidat	e number		

You may refer to the Chemistry Data Booklet for Higher and Advanced Higher.

Total marks — 110

SECTION 1 — 25 marks

Attempt ALL questions.

Instructions for the completion of Section 1 are given on page 02.

SECTION 2 — 85 marks

Attempt ALL questions.

Write your answers clearly in the spaces provided in this booklet. Additional space for answers and rough work is provided at the end of this booklet. If you use this space you must clearly identify the question number you are attempting. Any rough work must be written in this booklet. You should score through your rough work when you have written your final copy.

Use **blue** or **black** ink.

Before leaving the examination room you must give this booklet to the Invigilator; if you do not, you may lose all the marks for this paper.





The questions for Section 1 are contained in the question paper X813/77/02.

Read these and record your answers on the answer grid on page 03 opposite.

Use **blue** or **black** ink. Do NOT use gel pens or pencil.

- 1. The answer to each question is **either** A, B, C or D. Decide what your answer is, then fill in the appropriate bubble (see sample question below).
- 2. There is **only one correct** answer to each question.
- 3. Any rough working should be done on the additional space for answers and rough work at the end of this booklet.

Sample question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

- A fractional distillation
- B chromatography
- C fractional crystallisation
- D filtration.

The correct answer is \mathbf{B} — chromatography. The answer \mathbf{B} bubble has been clearly filled in (see below).



Changing an answer

If you decide to change your answer, cancel your first answer by putting a cross through it (see below) and fill in the answer you want. The answer below has been changed to **D**.

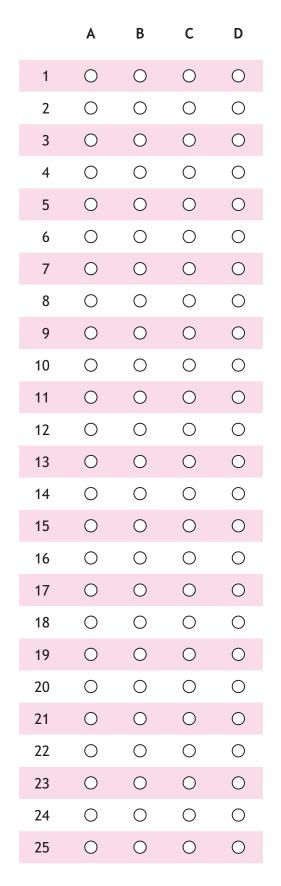


If you then decide to change back to an answer you have already scored out, put a tick (\checkmark) to the **right** of the answer you want, as shown below:









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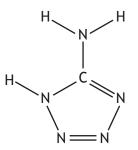


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1. (a) (continued)

- (iii) Distress flares also contain oxidising agents.
 - (A) Potassium perchlorate, $KClO_4$, can be used as the oxidising agent. Determine the oxidation state of chlorine in the perchlorate ion, ClO_4^{-} .
 - (B) In some distress flares, 5-aminotetrazole replaces perchlorate ions.



5-aminotetrazole

Determine the number of sigma bonds in a 5-aminotetrazole molecule.



1. (continued)

- (b) Oxygen candles can be used to supply oxygen in emergency situations.
 - (i) The initial energy required to start the oxygen candle can be provided by the combustion of iron.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Substance	$\Delta H_{\rm f}^{\circ}$ (kJ mol ⁻¹)	<i>S</i> ° (J K ^{−1} mol ^{−1})
Fe(s)	-	27.3
0 ₂ (g)	_	205
Fe ₂ O ₃ (s)	-824	87.4

Using information from the table, calculate

(A) ΔH° , in kJ mol⁻¹

(B) ΔS° , in J K⁻¹ mol⁻¹

(C) the temperature, in K, below which the reaction is feasible.

2

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[Turn over



1.	(b)	(cont	cinued)	MARKS	DO NOT WRITE IN THIS MARGIN	
		(ii)	Some oxygen candles contain sodium chlorate, NaClO ₃ , which decomposes at high temperatures to produce oxygen.			
			1.00 mol NaClO ₃ decomposes to produce 36.0 litres of O ₂ and an average person consumes 0.380 litres of O ₂ per minute.			
			Calculate the minimum mass of sodium chlorate required to supply oxygen to 5 people for 8 hours.	2		



[Turn over for next question

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2. The equation for the reaction between mercuric chloride and oxalate ions is shown.

$$2 HgCl_2(aq) \ + \ C_2O_4^{\ 2^-}(aq) \ \rightarrow \ 2 Cl^-(aq) \ + \ 2 CO_2(g) \ + \ Hg_2Cl_2(s)$$

In an experiment to determine the kinetics for this reaction the following results were obtained.

Experiment	[HgCl ₂] (mol l ⁻¹)	[C ₂ O ₄ ^{2–}] (mol l ⁻¹)	Initial rate of reaction (mol l ⁻¹ s ⁻¹)
1	0.0840	0.200	$0.860 imes 10^{-6}$
2	0.0840	0.400	$3.44 imes 10^{-6}$
3	0.0420	0.400	1.72 × 10 ⁻⁶
4	0.0320		2.11 × 10 ⁻⁶

- (a) Determine the order of the reaction with respect to
 - (i) HgCl₂

(b) Write the overall rate equation for the reaction.

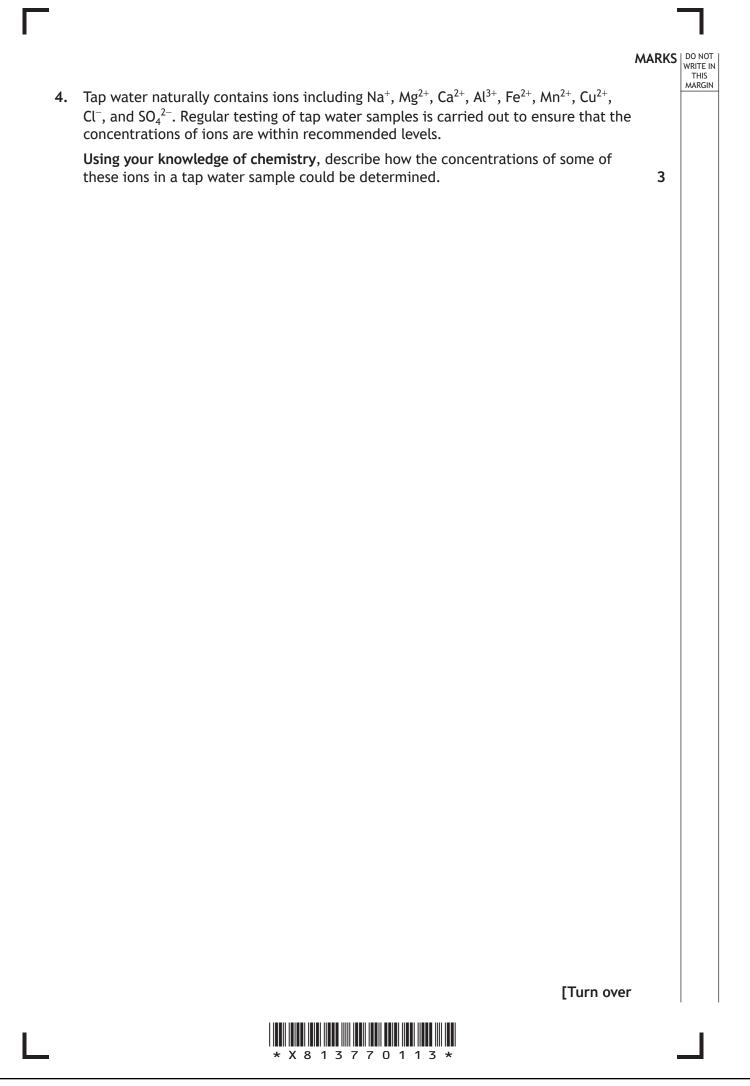


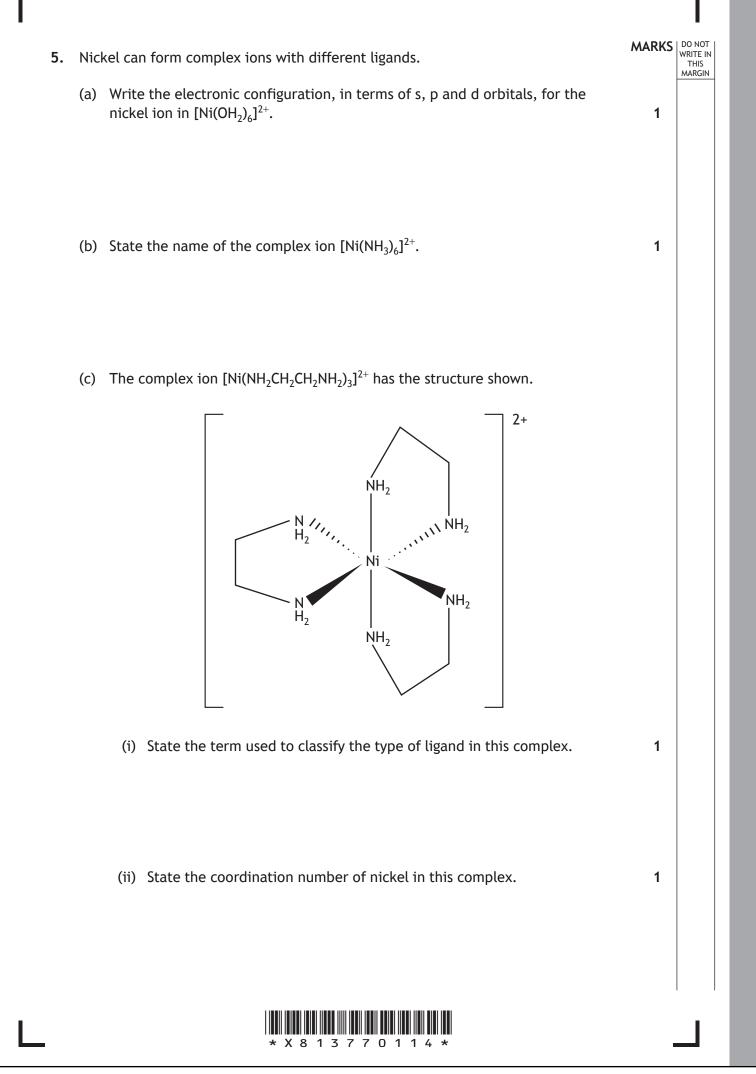
				MARKS	DO NOT WRITE IN THIS MARGIN
2.	(cont	inue	ed)		
	(c)	(i)	Calculate a value for the rate constant, <i>k</i> , including the appropriate units.	2	
		(ii)	Calculate the initial oxalate concentration, in mol l^{-1} , for experiment 4.	1	
			[Turn over		

MARKS | DO NOT WRITE IN 3. Oxalic acid occurs naturally in spinach leaves. The percentage by mass of oxalic THIS acid in spinach leaves was determined by soaking the leaves in water to dissolve the oxalic acid. The spinach leaves were removed from the mixture. Calcium chloride solution was then added to the oxalic acid solution to form a precipitate of calcium oxalate, as shown. $(COOH)_2(aq) + CaCl_2(aq) \rightarrow Ca(COO)_2(s) + 2HCl(aq)$ (a) The calcium oxalate precipitate was isolated by filtration. (i) Suggest what should be done to ensure the precipitation reaction has gone to completion. 1 (ii) The isolated precipitate was washed. State what else should be done to the precipitate before weighing to obtain an accurate mass. 1 (b) 8.975 g of spinach leaves produced 0.075 g of precipitate. 2 Calculate the percentage by mass of oxalic acid in the spinach leaves. (c) A source of information gives the percentage by mass of oxalic acid in spinach leaves as 0.97%. Suggest a reason for the difference between this quoted mass and your answer from part (b) above. 1

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X 8



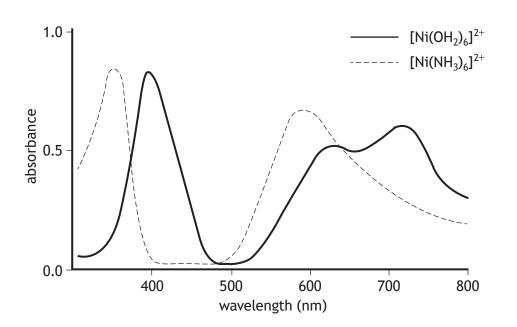




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- (d) Electron transitions involving the d subshell can give rise to colour in transition metal complexes.
 - (i) Explain fully why a solution of the complex ion $[Ni(OH_2)_6]^{2+}$ is green.

(ii) The graph shows the absorption spectra for solutions of the complex ions $[Ni(OH_2)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$.



Using information from the graph, explain which ligand has the greater ability to split d orbitals.





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. There	are many different compounds containing hydrogen and iodine.	
	lydrogen gas and iodine gas combine directly to form hydrogen iodide, HI(g). It constant temperature, an equilibrium is established.	
	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	
	(i) Write the expression for the equilibrium constant, <i>K</i> .	1
	(ii) 0.25 moles of $H_2(g)$ and 0.25 moles of $I_2(g)$ were mixed in a sealed 1.0 litre reaction vessel. At equilibrium, 0.015 moles of $I_2(g)$ were present.	
	Calculate the equilibrium constant, <i>K</i> , for this reaction.	2
((iii) The rate of the reaction between $H_2(g)$ and $I_2(g)$ can be increased using light of wavelength 578 nm.	
	Calculate the energy, in kJ mol ⁻¹ , of light corresponding to this wavelength.	2



6. (continued)

(b) Hydroiodic acid, HI(aq), was prepared from iodine, $I_2(aq)$, and hydrogen sulfide, $H_2S(g)$.

 $I_2(aq) + H_2S(g) \rightarrow 2HI(aq) + S(s)$

Hydrogen sulfide gas was bubbled through 250 cm³ of a solution containing 285 g of iodine. When the reaction was complete, the product mixture was separated by vacuum filtration and the filtrate was purified by distillation.

(i) Name the type of funnel that should be used to carry out vacuum filtration.

(ii) The distillate contained 251 g of HI.Calculate the percentage yield for this reaction.

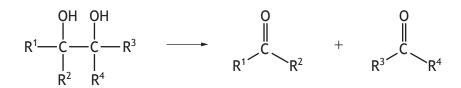
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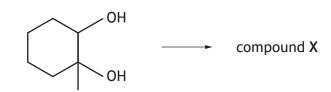
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6. (continued)

(c) Periodic acid, H_5IO_6 , can be used to oxidise diols with neighbouring hydroxyl groups into two aldehyde or ketone molecules.



The same oxidation reaction with 1-methylcyclohexane-1,2-diol and periodic acid gives only one product, compound **X**.



1-methylcyclohexane-1,2-diol

Draw a structural formula for compound X.



MARKS DO NOT WRITE IN THIS MARGIN 7. Oceans are essential in reducing the concentration of carbon dioxide in the atmosphere. Around half of the carbon dioxide produced by burning fossil fuels dissolves in the surface water of oceans. (a) Carbon dioxide dissolves in water to form carbonic acid, $H_2CO_3(aq)$. $H_2O(\ell) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \qquad \Delta H - ve$ Explain the effect rising seawater temperatures will have on the concentration of CO_2 dissolved in the oceans. 1 (b) Carbonic acid, $H_2CO_3(aq)$, dissociates as shown. $H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ $pK_a = 6.35$ (i) Explain how the strength of carbonic acid compares with that of ethanoic acid. 1 1 (ii) State the role of H_2O in the above equilibrium. [Turn over

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X 8

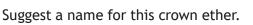
			MARKS	DO NOT WRITE IN THIS MARGIN
7.	(cor	ntinued)		
	(c)	The average pH of pre-industrial ocean surface water is recorded to be 8.2. The increased CO_2 dissolved in the oceans has already reduced the pH of surface water and by the year 2100 the pH is predicted to be 7.9.		
		(i) Calculate the concentration, in mol l^{-1} , of hydronium ions, H_3O^+ , in surface water with a pH of 8.2.	1	
		(ii) Calculate the percentage increase in hydronium ion concentration between water with a pH of 8.2 and water with a pH of 7.9.	2	
		Acid in the accors reacts with constalls containing calcium carbonate		
	(D)	Acid in the ocean reacts with seashells containing calcium carbonate. The percentage composition of calcium carbonate in seashells can be determined by carrying out a back titration using standard solutions of hydrochloric acid and sodium hydroxide.		
		(i) Outline the steps that would be needed to carry out this back titration.	2	
		(ii) Name a suitable control substance that could be used to validate this procedure.	1	
				I
		* X 8 1 3 7 7 0 1 2 0 *		

8. Crown ethers are a group of cyclic organic compounds.

(a) Crown ethers act as ligands and form complexes with alkali metal ions according to their size. They have names indicating the total number of atoms in the ring and the number of oxygen atoms.

One example of a crown ether is 18-crown-6, which is used to form complexes with K⁺ ions.



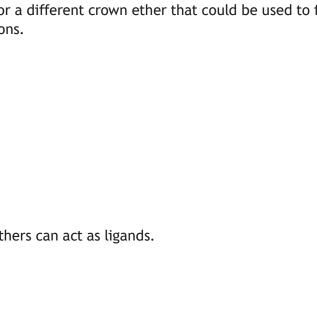


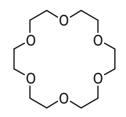
(ii) Draw a structure for a different crown ether that could be used to form a complex with Li⁺ ions.

(iii) State why crown ethers can act as ligands.

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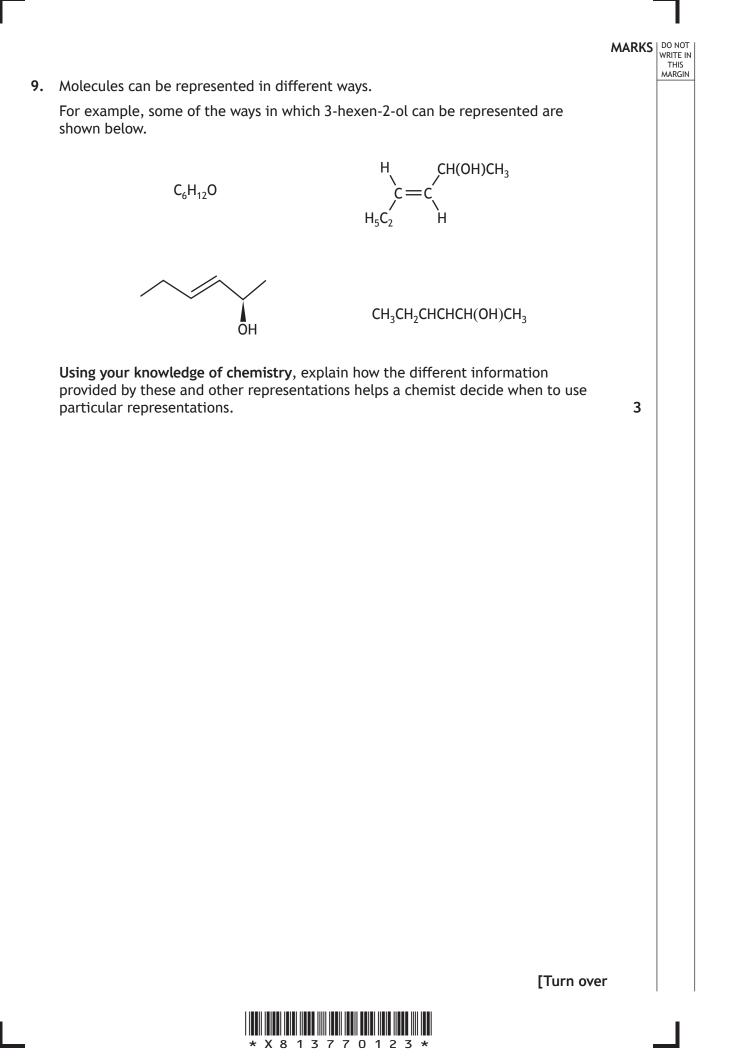
(continued)

OH

8.

1 3 7 7 0 1 2 2

X 8



MARKS DO NOT WRITE IN THIS MARGIN Cyclohexene is a cycloalkene. 10. (a) Cyclohexene can be synthesised by an addition reaction between buta-1,3-diene and ethene. (i) Buta-1,3-diene has a conjugated system. State what is meant by the term conjugated system. 1 (ii) State the type of hybridisation that is adopted by the carbon atoms in buta-1,3-diene. 1 (iii) A similar addition reaction can be used to make another cyclic compound. CN Draw a structural formula for the product of this reaction. 1 X 8 1 3 7 7 0 1 2 4

				MARKS	DO NOT WRITE IN THIS MARGIN
10.	(cor	ntinue	d)		
	(b)	Cyclo	hexene reacts with Cl ₂ to form 1,2-dichlorocyclohexane.		
		(i)	In the first step of the reaction, Cl_2 molecules become polarised. Explain why Cl_2 molecules become polarised.	1	
		(ii)	Draw a structural formula for the intermediate formed when cyclohexene reacts with Cl ₂ .	1	
		(iii)	1,2-dichlorocyclohexane has geometric isomers and optical isomers. (A) Explain why 1,2-dichlorocyclohexane has geometric isomers.	1	
			(B) Draw a cyclic isomer of 1,2-dichlorocyclohexane that does not have an optical isomer.	1	
			[Turn over		
_			* X 8 1 3 7 7 0 1 2 5 *	-	

10.	(coi	ntinue	d)	MARKS DO NOT WRITE IN THIS MARGIN	
	(c)		reaction between cyclohexene and HCl produces chlorocyclohexane.		
		(i)	Using structural formulae and curly arrow notation, outline the mechanism for this reaction.	2	
		(ii)	HCl has a permanent dipole. The size of a dipole is measured by its dipole moment and depends on the partial charge of the atoms and the bond length.		
			Dipole moment can be measured in units of Coulomb metres, Cm, or Debyes, D, and can be calculated using the following equations.		
			$\mu = Qr$ and $Q = partial charge \times e$		
			where: μ is the dipole moment in Coulomb metres, Cm		
			Q is the charge in Coulombs, C		
			r is the bond length in metres, m		
			$e = 1.60 \times 10^{-19} C$		
			$1 \text{ D} = 3.34 \times 10^{-30} \text{ Cm}$		
			Calculate the dipole moment, in D, of a hydrogen chloride bond, if the partial charge is 0.178 and the bond length is 0.127 nm.	2	



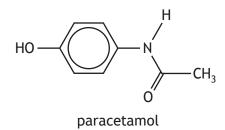
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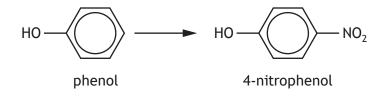


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11. Paracetamol can be synthesised in several reaction steps.

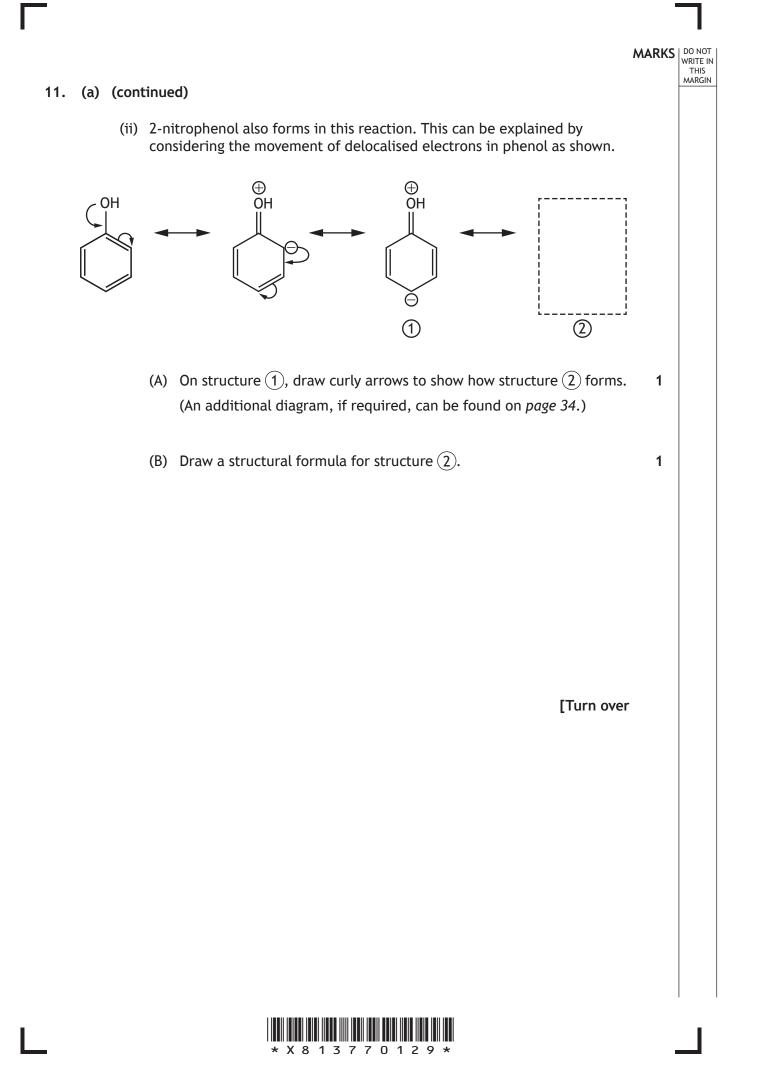


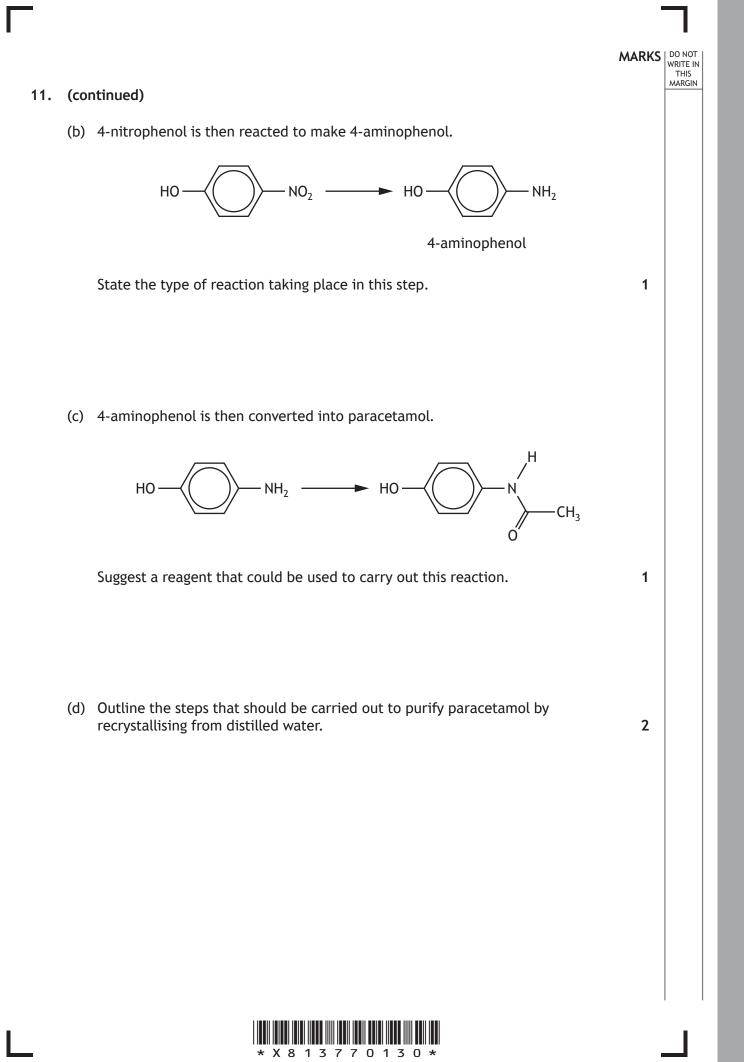
(a) The first step is conversion of phenol into 4-nitrophenol as shown.



(i) Write a formula for the electrophile in this reaction.

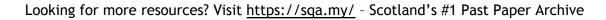






(continued) (e) Infrared spectroscopy and ¹H NMR spectroscopy were used to confirm that paracetamol had been synthesised. (i) The infrared spectrum of the recrystallised paracetamol is shown below. 100 transmittance (%) 50 0 4000 3000 2000 1500 1000 wavenumber (cm⁻¹) (A) The peak at wavenumber 1660 cm⁻¹ provides evidence that paracetamol has been synthesised. Suggest the bond in paracetamol that gives rise to this peak. 1 (B) By considering the functional groups present in paracetamol, suggest why the peaks that occur above 3000 cm⁻¹ are difficult to assign to specific bonds. 1 [Turn over

11.



0 1 3

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X 8 1 3 7 7

MARKS WRITE IN THIS MARGIN

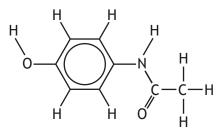
11. (e) (continued)

(ii) Analysis of a high resolution ¹H NMR spectrum of the recrystallised paracetamol gave the following information.

Chemical shift (ppm)	Height of integration curve (mm)	Type of multiplet
2.1	50	singlet
6.7	33	
7.3	33	
9.1	17	singlet
9.8	17	singlet

(A) Circle the proton environment on the structure below that is responsible for the peak at 2.1 ppm.

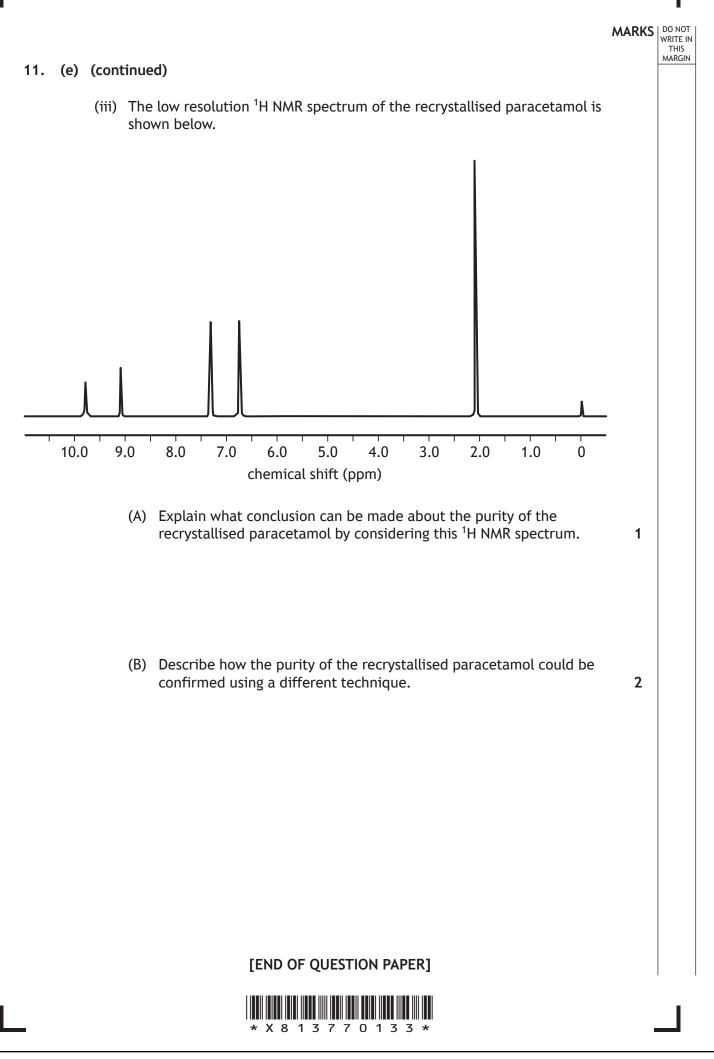
(An additional diagram, if required, can be found on page 34.)



(B) Complete the table by naming the multiplets that would be seen for the peaks at 6.7 and 7.3 ppm.

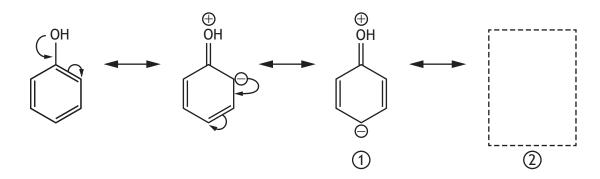
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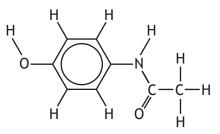


ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

Additional diagram for use with question 11 (a) (ii) (A)



Additional diagram for use with question 11 (e) (ii) (A)





ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK



ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK



ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK



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